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Role of Amorphous Phases in Enhancing Performances of Electrode Materials for Alkali Ion Batteries

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As one of the most competitive energy storage systems owing to their high energy density, conversion efficiency, long lifetime, and environment friendliness, alkali ion batteries have been widely used and continue to exhibit their potential to be the crucial components of future energy technologies. To further improve electrochemical performances of alkali ion batteries, great efforts have been put into the development of advanced electrode materials. However, scientists are facing great challenges in developing superior electrode materials due to the limitation of the existing technologies. Therefore, we recently chose a different route, that is, the amorphization engineering, to develop high-performance electrodes. Here, we review some recent studies about the role of amorphous phases in promoting electrochemical performances of both cathodes and anodes for alkali ion batteries. In addition, we review some progress in revealing the microscopic mechanisms of the increased ionic/electronic transport as well as the enhanced structural stability in electrodes, achieved by amorphization engineering.

Keywords: electrode materials, amorphization engineering, electrochemical performance, lithium ion batteries, sodium ion batteries, glass

INTRODUCTION

Energy storage technology is located at an important position in modern society because of its necessity in many fields, such as smart grids, electric vehicles, and electronics (Lee et al., 2014; Larcher and Tarascon, 2015; Liu et al., 2015). Among various energy storage systems, lithium ion batteries (LIBs) have been widely applied owing to their high-energy density, conversion efficiency, and long lifetime (Goodenough and Park, 2013; Manthiram et al., 2014; Lee et al., 2018; Zhan et al., 2018). Besides, sodium ion batteries (SIBs), another family of alkali ion batteries (AIBs), also drew much research interest in the past decade because of the similar properties to those of LIBs, the high abundance and low cost of sodium reserves (Pan et al., 2013; Yabuuchi et al., 2014; Xiang et al., 2015). However, with the fast development of science and technology, the electrochemical performances of these AIBs are encountering a bottleneck to be further improved for the growing requirement of many new application fields. Therefore, further improving the electrochemical performances of AIBs is the continuous pursuit of scientists and engineers.

To further enhance the electrochemical performances of AIBs, great efforts have been focused on the fabrication of new nanostructures in electrode materials through the atomic-scale design strategy during the past decades (Kang and Ceder, 2009; Sun Y. K. et al., 2012; Zhang et al., 2014; Xiong et al., 2015; Qing et al., 2016; Deng et al., 2017; Wei et al., 2017). However, another important

strategy, i.e., amorphization engineering, recently received much attention considering the unique functionalities of amorphous phases (Liu et al., 2012; An et al., 2014; Fang et al., 2014; Mathew et al., 2014; Kim et al., 2015; Nakata et al., 2016; Zhou et al., 2017; Wei et al., 2018; Zhang et al., 2018, 2019; Xiong et al., 2019). For example, the electrochemical performances of crystalline host materials relatively rely on various factors, such as the available energetically equivalent sites for guest-ion occupation/transport, crystal orientation, structural stability, phase transition, the spatial dimension of ion migration, defects in crystal, and the stoichiometric limitation of ion insertion (Liu et al., 2015; Xiang et al., 2015; Deng et al., 2017; Wang et al., 2018). Compared to those crystalline electrodes, the amorphous counterparts could deliver much improved specific capacities and long-term cyclability over a wide potential window (Mathew et al., 2014; Wei et al., 2018; Zhang et al., 2019). This is because the amorphous phases exhibit several advantages, such as improved ionic intercalation/deintercalation kinetics due to the existence of percolation pathways, a larger free volume, and higher specific surface area to accommodate lattice distortions.

Various routes can be applied to amorphize or vitrify the corresponding crystal materials. Besides the conventional melt-quenching method (Nakata et al., 2016; Zhang et al., 2018; Fan et al., 2019), there are many other techniques such as ball milling (Kapaev et al., 2017; Xiong et al., 2019), electrochemically induced amorphization (Kim et al., 2015; Rahman et al., 2017; Liu et al., 2018), sol-gel (Fang et al., 2014; Mathew et al., 2014), and magnetron sputtering (Baranchugov et al., 2007; Shi et al., 2009). Here we focus on only three techniques for amorphization: melt quenching, mechanochemical ball milling, and electrochemically induced amorphization. We give a short review about the recent progress in developing high-performance electrode materials for AIBs by means of amorphization engineering. We also describe the microscopic mechanisms of the amorphization-induced enhancement of electrochemical performances. Finally, we point out the perspectives in developing the superior electrode materials via amorphization.

AMORPHOUS PHASE IN NaFePO₄-BASED CATHODE

Owing to the excellent structural stability of polyanions, many types of phosphates have been considered to be promising cathode materials for AIBs (Padhi et al., 1997; Masquelier and Croguennec, 2013; An et al., 2015; Xiong et al., 2017; Yin et al., 2017). For example, olivine LiFePO₄, a typical representative of phosphate cathode materials, is one of the best cathode materials for LIBs (Padhi et al., 1997; Zhang et al., 2014; Guo et al., 2015). However, maricite NaFePO₄, thermodynamically stable sodium analog of LiFePO₄, delivers low sodium storage activity due to the absence of sodium-ion diffusion channels (Zaghib et al., 2011; Prosini et al., 2014). Some traditional strategies, e.g., increasing work temperature (Zaghib et al., 2011), carbon coating (Sun A. et al., 2012), and reducing grain size (Prosini et al., 2014), have been employed to modify the electrochemical performances of maricite NaFePO₄, but the enhancement is still not satisfying.

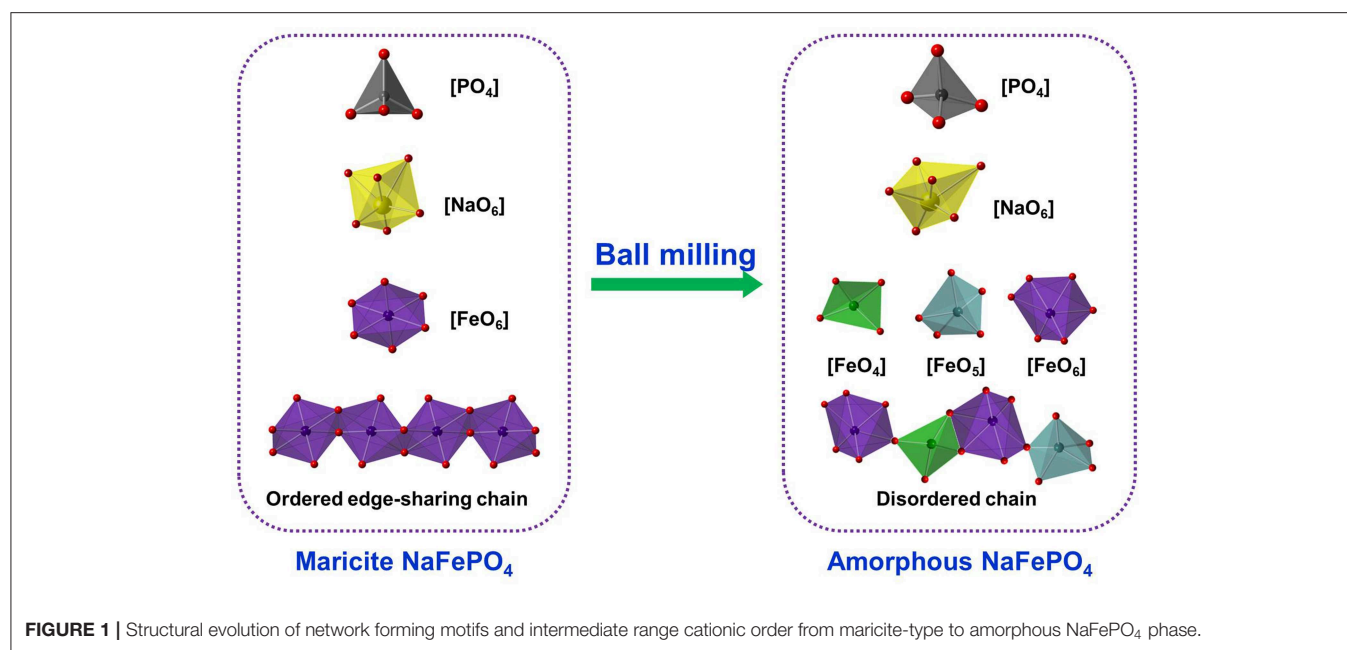
Thus, it is necessary to find an alternative better strategy for enhancing the sodium storage performance of NaFePO₄.

Recently, through amorphization, an important breakthrough was achieved in enhancing the Na-storage performance of maricite-type NaFePO₄ (Kim et al., 2015; Rahman et al., 2017; Liu et al., 2018; Xiong et al., 2019). Unexpectedly, after desodiation at high potential (4.5 V vs. Na⁺/Na) for 5 h, the maricite NaFePO₄ exhibited a high reversible sodium storage capacity of 142 mA h g⁻¹ at C/20 without obvious decay after 200 cycles (Kim et al., 2015). Based on the X-ray diffraction, extended X-ray absorption fine structure, and high-resolution electron transmission microscopy technologies, the transformation of maricite NaFePO₄ into amorphous FePO₄ after the prime high-potential desodiation process was observed, which could be responsible for the greatly enhanced electrochemical performances. Compared to the directly synthesized amorphous FePO₄, the amorphous phase transformed from the maricite NaFePO₄ shows high structural stability that benefits the ion storage (Liu et al., 2012; Fang et al., 2014). Understanding of the amorphization process is crucial for elucidating the atomistic-scale structural origin of the above-mentioned phenomenon.

Following this observation, other optimization strategies were also applied to further improve the electrochemical performances of electrochemically induced amorphous NaFePO₄, such as graphene modification, minimizing particle size and carbon cloth loading (Rahman et al., 2017; Liu et al., 2018; Ma et al., 2019). Combination of electrochemically induced amorphization with nanostructure design led to excellent electrochemical performances for various kinds of maricite NaFePO₄-based nanocomposites. Notably, Liu et al. (2018) fabricated maricite NaFePO₄ nanoparticles with minimized grain size (about 1.6 nm) embedded in carbon nanofibers via electrospinning technique. Using this approach, along with the electrochemically induced amorphization, they achieved high rate performance (61 mA h g⁻¹ at 7500 mA g⁻¹, i.e., at 50 C) and excellent cycling stability (capacity retention of about 89% after 6300 cycles).

In addition, the most widely used amorphization method, i.e., melt-quenching method, also has been attempted to attain amorphous NaFePO₄ (Nakata et al., 2016). Unfortunately, the NaFePO₄ (50FeO·50NaPO₃) glass has not been successfully prepared due to the strong crystallization tendency of its melt. However, the 40FeO·60NaPO₃ glass was obtained, which exhibits a capacity of 115 mA h g⁻¹ at 0.1 C when evaluated as a cathode material for SIBs, demonstrating the sodium storage activity of FeO-NaPO₃ glasses. Moreover, some glass-ceramic electrode materials were obtained via melt-quenching method, which also display excellent electrochemical performances (Honma et al., 2012, 2013, 2014; Tanabe et al., 2018). In these electrodes, the crystal phases play a dominant role in enhancing the electrochemical activity. However, there is a lack of in-depth investigations with respect to the role of glass phases.

Employing another amorphization approach, i.e., mechanochemical ball milling, we attempt to obtain amorphous NaFePO₄ (Xiong et al., 2019). Systematic calorimetric characterizations indicate that the glass transition was not observed prior to the sharp crystallization peak, verifying



that NaFePO₄ is a poor glass former, coinciding with the failure in preparing NaFePO₄ glass through melt-quenching method (Nakata et al., 2016). Through adjusting the ball-milling parameters, a series of NaFePO₄ composites with different fractions of amorphous phase (i.e., with different ratios of crystal to amorphous phases) were fabricated. The detailed characterizations of electrochemical performances confirmed the positive correlation between the amorphous degree and sodium storage capacity. However, the nanocrystals embedded in amorphous NaFePO₄ matrix also play a key role in boosting the structural stability, leading to an enhancement of cycling stability. Also, the optimized NaFePO₄ composite delivers an initial capacity of 115 mA h g⁻¹ at 1 C (155 mA g⁻¹) with capacity retention of 91.3% after 800 cycles. Furthermore, systematic structural characterizations, such as the X-ray absorption near edge and Raman spectroscopy, were performed to reveal the atomic-scale structural evolution of NaFePO₄ from crystalline to amorphous phase (Xiong et al., 2019). For example, according to the O K-edge X-ray absorption near edge spectra, the decrease of the nearest coordination number of oxygen was verified after amorphization. As shown in **Figure 1**, upon amorphization, the relatively symmetrical FeO₆ octahedra become distorted Fe–O polyhedra, such as mainly octahedra, pentahedra, and tetrahedra, while the isolated P–O tetrahedral units remain unaffected (Xiong et al., 2019). Possibly due to the relatively weaker bonding strength of Fe–O bonds compared to the P–O ones, the nearest coordination environment of Fe could be easier to be altered than that of phosphorus. The above-mentioned evolution in the local surroundings of iron and oxygen could result in the statistical distortion and asymmetry of sodium sites, and thus enhances the potential energy and instability of sodium sites and decreases the activation barriers of sodium-ion diffusion. Therefore, these work further revealed the

functionalities of both amorphous and crystal phases together with their atomistic-scale mechanism.

GLASS PHASE IN V₂O₅-TeO₂ GLASS-BASED ANODE

Glass-based anodes for LIBs, especially Sn-based glassy materials, have attracted much attention (Courtney, 1997; Idota et al., 1997; Machill et al., 1999; Morimoto et al., 1999, 2001; Goward et al., 2000; Lee et al., 2000; Hayashi et al., 2004; Kebede et al., 2018). For instance, the Sn_{1.0}Bo_{0.56}Po_{0.42}Al_{0.42}O_{3.6} glass-based anode displayed a capacity retention of 90% after 100 cycles, which is better than that of SnO powder (Idota et al., 1997). However, the other Sn-based glass anodes exhibited poor cycling stability (Courtney, 1997; Machill et al., 1999; Lee et al., 2000; Morimoto et al., 2001). The metallic Sn clusters could precipitate from the Sn-based glass and aggregate during the charging/discharging process, leading to fast capacity fading (Courtney, 1997; Machill et al., 1999; Lee et al., 2000). To alleviate the capacity fading, much work was done, e.g., adjusting the charging/discharging voltage range and modifying the composition, while the achieved cycling stability is still unsatisfied (below 50 cycles) (Courtney, 1997; Lee et al., 2000; Morimoto et al., 2001; Hayashi et al., 2004). Therefore, it is a big challenge to further improve the cyclability of glass-based anodes. Encouragingly, some important improvements were obtained in some recent studies (Zhang et al., 2018, 2019; Fan et al., 2019).

Recently, utilizing its attractive lithium storage ability and high electronic conductivity (Dhawan et al., 1982; Levy et al., 1989; Levy and Souquet, 1989; Kjeldsen et al., 2013; Fan et al., 2019), Zhang et al. investigated the V₂O₅-TeO₂ glass system as anode materials and achieved a breakthrough in

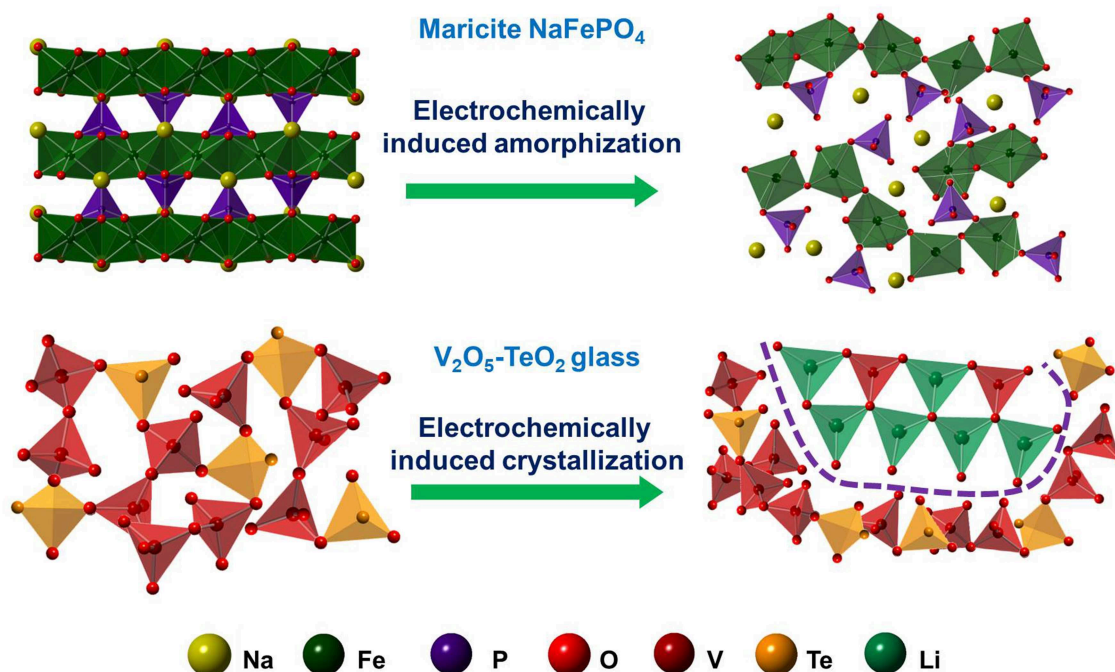


FIGURE 2 | Schematic diagram of structural evolution of electrochemically induced amorphization (maricite-type phase NaFePO_4 as an example) or crystallization ($\text{V}_2\text{O}_5\text{-TeO}_2$ glass as an example).

enhancing the cycling stability (Zhang et al., 2018, 2019). In contrast to the electrochemically induced amorphization in maricite NaFePO_4 , the electrochemically induced nanocrystals was observed in the $\text{V}_2\text{O}_5\text{-TeO}_2$ glass-based anode (**Figure 2**) (Zhang et al., 2018). Even during the first discharge process, the nanocrystals precipitate in the glass matrix and gradually grow upon the subsequent cycles. The nanocrystals are uniformly distributed in glass matrix and play an important role in stabilizing the structure. Hence, during the long-term discharging/charging cycling process, this stable structure can maintain, resulting in an enhanced cycling stability. In addition, the electrochemical impedance spectroscopy plots imply that the electronic conduction and lithium-ion diffusion in $\text{V}_2\text{O}_5\text{-TeO}_2$ glass-based anode could be promoted after 1,000 cycles compared to the pristine one. Benefiting from the synergistic effects of nanocrystals and glass matrix, the $\text{V}_2\text{O}_5\text{-TeO}_2$ glass-based anode displays significantly improved cycling stability and excellent rate performance. The reversible capacity of the optimized glass-based anode with the composition $60\text{V}_2\text{O}_5\text{-}40\text{TeO}_2$ still remained about 132 mA h g^{-1} after 1,000 cycles at $1,000 \text{ mA g}^{-1}$.

The above-mentioned work demonstrates the crucial effect of nanocrystals embedded in glass on electrochemical performances of $\text{V}_2\text{O}_5\text{-TeO}_2$ glassy anode. However, both the nanocrystal formation and the detailed mechanism of the enhancement of electrochemical performances still need to be understood. Therefore, to do so, further efforts were made in another study (Zhang et al., 2019). The enthalpy relaxation behaviors of fast-quenched $60\text{V}_2\text{O}_5\text{-}40\text{TeO}_2$ glass confirmed its high structural and energetic heterogeneity. The high-energy domains are

vulnerable to the insertion/extraction of lithium ions. Thus, these domains are easily converted to the ordered ones, driven by the decrease of the Gibbs free energy. In addition, more free space could occur as a result of the volume shrinkage caused by the nanocrystal formation, especially in the interphase between nanocrystals and glass matrix, thereby enhancing both the storage and the diffusion of lithium ions. In addition, during the long-term cycling process, the nanocrystals transform from the LiVO_3 phase to the electrochemically active $\gamma\text{-Li}_3\text{VO}_4$ phase, and after 5000 cycles, the latter phase becomes the dominating one, which has higher ionic conductivity. Consequently, the $60\text{V}_2\text{O}_5\text{-}40\text{TeO}_2$ glass-based anode exhibits excellent rate performance. On the other hand, the enhanced cycling stability of $60\text{V}_2\text{O}_5\text{-}40\text{TeO}_2$ glass-based anode is associated with the strengthened structure. The glass matrix can buffer the volume variation during the repeated insertion/extraction of lithium ions due to the open network structure. Moreover, the nanocrystals and the free space between nanocrystals and glass matrix could play a critical role in hindering the propagation of the micro-cracks.

Furthermore, the type of the discharging/charging-induced nanocrystals depends on the glass composition. For $50\text{TeO}_2\text{-}50\text{V}_2\text{O}_5$ glass doped with 5 mol% Al_2O_3 , the metallic Te nanocrystals could be generated from the glass matrix upon the discharging/charging cycles, and hence, the electrochemical performances of this Al_2O_3 -doped glass are highly different from those of the above-mentioned $\text{V}_2\text{O}_5\text{-TeO}_2$ glass (Fan et al., 2019). Interestingly, this nanocrystal/glass composite also possesses excellent cycling stability. After 1,000 cycles at $1,000 \text{ mA g}^{-1}$, the capacity of 202 mA h g^{-1} was also remained.

OUTLOOK AND PERSPECTIVES

We have reviewed recent advances in developing electrode materials for AIBs by amorphization engineering. The positive effects of amorphization engineering on Li/Na ion storage and transfer kinetics of electrode materials were confirmed by several representative cases. Electrochemically induced amorphization and nanocrystal formation were observed in NaFePO₄-based crystal cathode and V₂O₅-TeO₂ glass-based anode upon charging/discharging cycling, respectively. Interestingly, the nanocrystals in disordered matrix played an important role in enhancing the electrochemical performances of AIBs. In other words, tuning of order/disorder in electrodes can lead to considerable improvement of the AIB performances.

Despite the above-mentioned advances in developing electrode materials, several challenging problems still remain to be tackled. For NaFePO₄ cathodes, there is no direct evidence for the Na-storage mechanism of the nanocrystalline/amorphous composite. The synthesis of fully amorphous NaFePO₄ will be a crucial step for further understanding the effect of nanocrystals in amorphous matrix on the electrochemical performances of the cathodes for SIBs. For V₂O₅-TeO₂ glass-based anodes, the

formation mechanism of LiVO₃ and γ -Li₃VO₄ is still not fully clear. Moreover, the relation between the glass composition and the nanocrystal formation induced by the electrochemical cycles needs to be clarified. We still need to answer the question why the electrochemically induced amorphization or crystallization occurs in different electrode materials. Finally, the electrochemical performances of the electrode materials obtained by amorphization engineering should also be evaluated in the energy storage units, particularly regarding the initial Coulombic efficiencies, the specific capacity, and the energy density of AIBs.

AUTHOR CONTRIBUTIONS

FX was responsible for writing and formatting the article. HT and YY supervised and revised the manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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